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MATHEMATICS

On the Determinants of Wroński in Linear Rings

by

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Presented by T. WAŻEWSKI on June 25, 1956

1. In operational calculus [1] we consider the differential equations

$$x^{(n)} + a_{n-1}x^{(n-1)} + \ldots + a_0 x = 0, \tag{1}$$

in which a_j $(j=0,1,\ldots,n-1)$ are given elements of a field of operators, and x is the unknown function assigning operators to real numbers. Equations (1) contain, as a particular case, ordinary differential equations — linear, homogeneous, with constant coefficients. Thus the results presented in this paper are valid also in the theory of ordinary differential equations.

2. Let C denote a commutative ring with unity and K any commutative linear ring on C. Assume that a linear endomorphism on elements of K was defined, which transformes x into $x^{(1)}$ and in general $x^{(n)}$ into $x^{(n+1)}$ $(n=1,2,\ldots)$. Let $a_j \in C$ $(j=0,1,\ldots,n-1)$, $b_i \in C$ $(i=0,1,\ldots,k-1)$. Suppose that we know the linearly independent solutions of the equation

$$L_f x \equiv x^{(n)} + a_{n-1}x^{(n-1)} + \ldots + a_0 x = 0,$$

which corresponds to the polynomial $f(w)=w^n + a_{n-1}w^{n-1} + \ldots + a_0$ and the linearly independent solutions of the equation

$$L_g x \equiv x^{(k)} + b_{k-1}x^{(k-1)} + \ldots + b_0 x = 0,$$

which corresponds to the polynomial $g(w)=w^k + b_{k-1}w^{k-1} + \ldots + b_0$.

Let us form a third equation, $L_h x \equiv L_f(L_g x)=0$. What are the solutions of equation $L_h x=0$, and are they linearly independent? The answer to the second question is given by Theorem 2, valid in any linear space. The theorems on the determinants of Wroński have, incidentally, been proved and can also serve for the proof of linear independence of the

solutions of the equation $L_h x = 0$. The Theorems 1, 3 and 4 are valid in the ring K.

3. By the determinant of Wroński of the elements $y_1, \ldots, y_n$ we understand the determinant

$$\begin{vmatrix} y_1, \ldots, y_1^{(n-1)} \\ \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \\ y_n, \ldots, y_n^{(n-1)} \end{vmatrix}.$$

THEOREM 1. *If $y_1, \ldots, y_n$ are solutions of equation $L_f x = 0$ of "order" n, and $z_1, \ldots, z_k$ are solutions of equation $L_g x = 0$ of "order" k, both equations having unity as the "highest coefficient", then the determinant of Wroński W_h of the $(n+k)$ elements $y_1, \ldots, y_n$, $z_1, \ldots, z_k$ is equal to the product of the determinants of Wroński W_f of the elements $y_1, \ldots, y_n$ and W_g of elements $z_1, \ldots, z_k$ and the resultant $R_{g,f}$ of polynomials g and f:*

$$W_h = W_f \cdot W_g \cdot R_{g,f}.$$

4. Making use of the fact that $ax = 0$ $(a \in C,\ x \in K)$ only if $a = 0$ or $x = 0$, it is easy to prove the following theorem:

THEOREM 2. *If equations $L_f x = 0$ and $L_g x = 0$ with coefficients from an arbitrary *) commutative ring C have a common solution $x_1 \neq 0$, then $R_{f,g} = 0$ ($R_{f,g}$ is the resultant of polynomials f and g).*

If C is a ring which has no divisors of zero **), the vanishing of the resultant $R_{f,g}$ is equivalent to the polynomials f, g having a common factor of positive degree. In particular, the discriminant of an irreducible polynomial in a ring which has no divisors of zero or in the field C is different from zero.

Denote by $y_1, \ldots, y_n$ solutions of the equation $L_f x = 0$ and by $z_1, \ldots, z_k$ solutions of the equation $L_g x = 0$. If $y_1, \ldots, y_n$, $z_1, \ldots, z_k$ are linearly dependent, but $y_1, \ldots, y_n$ are linearly independent and $z_1, \ldots, z_k$ are also independent, then the equations $L_f x = 0$ and $L_g x = 0$ have a common solution $x_1 \neq 0$ and the resultant $R_{f,g}$ vanishes.

5. It is known [2] that if x_i $(i = 1, \ldots, n)$ satisfy the equation $L_f x = 0$ corresponding to the polynomial f, and if the linear operation A satisfies the condition $(Ax)^{(1)} = Ax^{(1)} + x$, then the elements $A^\varkappa x_i$ $(\varkappa = 0, 1, \ldots, k-1;\ i = 1, \ldots, n)$ satisfy the equation $L_{f^k} x = 0$, corresponding to the k-th power of the polynomial f.

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*) The ring C does not necessarily contain a unity. Theorem 2 is valid for arbitrary polynomials $f(w) = a_n w^n + \ldots + a_0$, $g(w) = b_k w^k + \ldots + b_0$.

**) In the ring of continuous real functions with ordinary addition and multiplication let us take $a \neq 0$, $b \neq 0$ such that $ab = 0$, $a \geqslant 0$, $b \geqslant 0$. The polynomials $f(w) = w^2 + a$, $g(w) = w^2 + bw + a$ are irreducible but $R_{f,g} = 0$.

The following theorem expresses the determinant

$$W_{f^k}=\begin{vmatrix} x_1, & x_1^{(1)} & , \dots , & x_1^{(nk-1)} \\ \dots & \dots & \dots & \dots \\ x_n, & x_n^{(1)} & , \dots , & x_n^{(nk-1)} \\ Ax_1, & (Ax_1)^{(1)} & , \dots , & (Ax_1)^{(nk-1)} \\ \dots & \dots & \dots & \dots \\ Ax_n, & (Ax_n)^{(1)} & , \dots , & (Ax_n)^{(nk-1)} \\ A^{k-1}x_1, & (A^{k-1}x_1)^{(1)} & , \dots , & (A^{k-1}x_1)^{(nk-1)} \\ \dots & \dots & \dots & \dots \\ A^{k-1}x_n, & (A^{k-1}x_n)^{(1)} & , \dots , & (A^{k-1}x_n)^{(nk-1)} \end{vmatrix}$$

by the k-th power of the determinant

$$W_f=\begin{vmatrix} x_1, \dots , x_1^{(n-1)} \\ \dots \\ x_n, \dots , x_n^{(n-1)} \end{vmatrix}.$$

THEOREM 3. *If $x_1, \dots , x_n$ are solutions of the equation*

$$L_f x \equiv x^{(n)} + a_{n-1}x^{(n-1)} + \dots + a_0 x = 0,$$

and for those x_i $(i=1, \dots , n)$ the conditions

$$(2) \qquad \begin{gathered} (Ax)^{(1)} = Ax^{(1)} + x \\ x^{(\mu)} \cdot A^p x^{(\nu)} = x^{(\nu)} \cdot A^p x^{(\mu)} \\ (p=1, \dots , k-1; \quad \mu, \nu = 0, 1, \dots , nk-1) \end{gathered}$$

are satisfied, then

$$W_{f^k} = [1!2! \dots (k-1)!]^n \cdot R_{f,f'}^{k(k-1)/2} \cdot W_f^k,$$

where $R_{f,f'}$ is the discriminant of the polynomial f.

The second of conditions (2) can, of course, be replaced by a somewhat stronger but simpler condition: $A(xy)=(Ax)y$.

6. An arbitrary polynomial $F(w)$ with coefficients from a ring having no divisors of zero may be decomposed into factors irreducible in this ring.

$$F(w) = \prod_{j=1}^{p} f_j^{\alpha_j}(w).$$

Let us take only those factors $f_j(w)$ to which correspond equations having solutions $x_{j1}, \dots , x_{jm_j}$ $(j=1, \dots , q)$, different from zero. By Theorem 2, from the linear independence of elements $x_{j1}, \dots , x_{jm_j}$ we can deduce the linear independence of elements $A^r x_{js}$ $(r=0, 1, \dots , \alpha_j - 1;\ j=1, \dots , q;\ s=1, \dots , m_j)$.

7. Suppose that $F(w)$ can be decomposed into the factors

$$f_j(w)=w^{n_j}+a_{n_j-1}w^{n_j-1}+\ldots+a_0$$

$$F(w)=c\prod_{j=1}^{q}f_j^{\alpha_j}(w).$$

Applying successively Theorems 1 and 3, we obtain a theorem from which it may be deduced that the linear independence of the solutions $x_{j1},\ldots,x_{jn_j}$ of the equations $L_{f_j}x=0$ implies the linear independence of $A^r x_{js}(r=0,1,\ldots,\alpha_j-1;\ j=1,\ldots,q;\ s=1,\ldots,n_j)$.

THEOREM 4. *If the assumptions of Theorems* 1 *and* 3 *are satisfied, then*

$$W_F=\prod_{j=1}^{q}[1!2!\ldots(\alpha_j-1)!]^{n_j}\cdot\prod_{1\leqslant\varkappa<\mu\leqslant q}R^{\alpha_\mu\alpha_\varkappa}_{f_\mu,f_\varkappa}\cdot\prod_{j=1}^{q}R^{\alpha_j(\alpha_j-1/2)}_{f_j,f_j'}\prod_{j=1}^{q}W^{\alpha_j}_{f_j}.$$

8. Theorem 4 contains as a particular case the result of J. Mikusiński [3]. In order to obtain this result, it must be assumed that the polynomial $F(w)$ can be decomposed into linear factors and that there exist elements x_j, different from zero, which satisfy equations $x^{(1)}=w_jx$ $(j=1,\ldots,q)$, w_j being the roots of polynomial $F(w)$ and the product of those x_j $(j=1,\ldots,q)$ being different from zero.

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MATHEMATICS

Note of the Representation of Large Integers as Sums of Primes

by

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Let $K(n)$ denote the number of primes such that the integer n is expressible as a sum of $K(n)$ but not as a sum of less than $K(n)$ primes. Shapiro and Warga [1] proved that $K(n) \leqslant 20$ for $n > N$. In this note it is shown that a slight improvement on their result is obtainable; actually we can prove that $K(2n) \leqslant 18$ and $K(2n+1) \leqslant 17$ for $n > N$. A sketch of the proofs is given below.

Let Σ be the set of all non-negative even integers and $A \subset \Sigma$. We define the "even" asymptotic density of A by

$$\delta_{\Sigma}^{*}(A) = \underline{\lim}_{n=\infty} \frac{A(2n)}{n},$$

where $A(x)$ denotes, as usual, the number of integers in A not exceeding x. Analogous to a known property of the asymptotic density [2] is the relation

$$\delta_{\Sigma}^{*}(A+B) \geqslant \delta_{\Sigma}^{*}(A) + \frac{k-1}{k}\,\delta_{\Sigma}^{*}(B), \tag{1}$$

provided that $A, B \subset \Sigma$, $\delta_{\Sigma}^{*}(A) + \delta_{\Sigma}^{*}(B) \leqslant 1$ and B contains a chain of k consecutive even integers.

Further, we may define the "even" average order in a way analogous to the ordinary average order. Then, if $0 \in B \subset \Sigma$, $A \subset \Sigma$, $\delta_{\Sigma}^{*}(A) = \alpha$ and λ^{*} is the even average order of B, we have

$$\delta_{\Sigma}^{*}(A+B) \geqslant \alpha\left(1 + \frac{1-\alpha}{\lambda^{*}}\right), \tag{2}$$

which is also analogous to a known result [3]. A further analogue to the known result is the relation

$$A+B\sim\Sigma, \tag{3}$$

provided that $A,B\subset\Sigma$ and $\delta_\Sigma^*(A)+\delta_\Sigma^*(B)>1$, where "$\sim$" denotes that the set on the two sides of (3) differ by only a finite number of elements.

The results (1), (2) and (3) can be justified by an argument of "isomorphism".

We use p and p' to denote odd primes only. It is known by [1], that for $M=\{p+p'\}$,

$$\lim_{x\to\infty}\frac{M(x)}{x}\geqslant\frac{1}{16}.$$

Now consider $P_0=\{p-3\}$, then $\delta_\Sigma^*(P_0+P_0)=\delta_\Sigma^*(M)$. It is easily verified that $2n\in P_0+P_0$ for $1\leqslant n\leqslant 125$. Hence by (4) and (1)

$$\delta_\Sigma^*(hM)=\delta_\Sigma^*\big(h(P_0+P_0)\big)\geqslant\operatorname{Min}\left\{\frac{1}{8}+\left(1-\frac{1}{125}\right)\frac{h-1}{8},1\right\},$$

where, of course, hA is an abreviation for $A+\ldots+A$ (h terms). Thus,

$$\delta_\Sigma^*(8M)+\delta_\Sigma^*(M)=\delta_\Sigma^*\big(8(P_0+P_0)\big)+\delta_\Sigma^*(2P_0)>1.$$

From (3) we find that

$$\Sigma\sim 9M\sim 9(P_0+P_0).$$

It follows that every sufficiently large even integer can be expressed as a sum of at most 18 primes and also that the even average order of P is $\lambda^*\leqslant 18$. So, in view of (2), we have

$$\delta_\Sigma^*(M+P_0)\geqslant\tfrac{1}{8}\left(1+\frac{1-\frac{1}{8}}{18}\right),$$

and hence

$$\delta_\Sigma^*(7M)+\delta_\Sigma^*(M+P_0)>1+\frac{7}{8\cdot 8\cdot 18}-\frac{6}{8\cdot 125}>1\ ^*).$$

Therefore, by (3),

$$\Sigma\sim 8M+P_0$$

A moment of consideration shows that every large odd integer is expressible as a sum of at most 17 primes.

It should be noted that our result is far weaker than what can be deduced from the famous Goldbach-Vinogradov theorem, namely $K(n)\leqslant 4$ for sufficiently large n. Our proof, however, is elementary in the sense

*) The same result can also be obtained by using an analogue of Erdös'result instead of that of Kasch's.

that we make no use of any deep analytic method or theorem. Besides what can be seen from the note itself, our proof depends indirectly upon Selberg's sieve method which may also be regarded as elementary.

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MATHEMATICS

On Algebraic Structures and Homotopy Invariants

by

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Let X be a geometric object. According to the geometric properties of X a lot of algebraic structures are constructed to "realise" them. For instance, in a Euclidean space we have parallel lines in a given direction, — this property evidently determines a translation group (in the given direction) whose trajectories are the given parallel lines. It is interesting in history to study the algebraic properties of the algebraic structures associated with a geometric object. This is the fundamental ideal of algebraic topology.

In 1935, W. Hurewicz [1] introduced homotopy types of topological spaces. Afterwards J. H. C. Whitehead defined cohomology rings [2] and cohomology systems [3]. He produced a $1-1$ correspondence between isomorphism classes of cohomology rings and the homotopy types of simply connected 4-dimensional polyhedra and then he simplified his argument to establish a similar correspondence between isomorphism classes of cohomology systems and A_n^2-polyhedra ($n \geqslant 3$). According to Whitehead an arcwise connected polyhedron, K, is called an A_n^2-polyhedron if $\dim K \leqslant n+2$ and $\pi_r(K)=0$, $r=1,\ldots,n-1$. We assume $n \geqslant 3$. Let H^n, H^{n+1}, H^{n+2} be additive groups, each of which has a finite number of generators, H^n being free. A new group, $H^n(2)$, is defined as the direct sum *)

$$H_2^n + \Delta^*({}_2H^{n+1}),$$

where $\Delta^*({}_2H^{n+1})$ is the image of ${}_2H^{n+1}$ under an isomorphism Δ^*. Here Δ^* is determined modulo an arbitrary homomorphism

$${}_2H^{n+1} \to H_2^n.$$

*) Let G be an additive Abelian group then $G_2 = G - 2G$, and ${}_2G$ is the subgroup of G which consists of all the elements g, such that $2g=0$.

In other words, the isomorphism Δ^* is not determined uniquely, but there is a uniquely determined homomorphism

$$\Delta: H^n(2) \to {}_2H^{n+1},$$

such that $\Delta\Delta^* = 1$ and $\Delta^{-1}(0) = H_2^n$. Furthermore, a homomorphism $\mu: H^r \to H^r(2)$, $(r = n, n+2)$, onto H_2^r is defined in the usual way. Finally, there is given a homomorphism $\gamma^*: H^n(2) \to H^{n+2}(2)$, which may be arbitrary. Then H^n, H^{n+1}, H^{n+2}, $H^n(2)$, $H^{n+2}(2)$, together with Δ, μ and γ^* constitute an A_n^2-cohomology system. This is the algebraic cohomology system of J. H. C. Whitehead. On the other hand, if an A_n^2-polyhedron, K, is given, we have the integral cohomology groups $H^r(r = n, n+1, n+2)$ and the cohomology groups $H^r(2)$, $(r = n, n+2)$ with integers reduced mod. 2 as coefficients, and we take the natural homomorphism μ, $\Delta = \frac{1}{2}\delta$ and finally γ^* as the Steenrod square [4] $\gamma^* x = x \cup_{n-2} x_\varepsilon H^{n+2}(2)$, where $x_\varepsilon H^n(2)$. Therefore a cohomology system is associated with K. A homomorphism f between two cohomology systems contains five homomorphisms of the corresponding groups with a restriction that f commutes with μ, Δ and γ^*. Particularly f is called a (μ, Δ)-homomorphism if f commutes with μ and Δ only.

Now cohomology groups are invariants of homotopy type. How many different homotopy types of A_n^2-polyhedra may there be if their cohomology groups are assigned? In other words, we are required to study the algebraic properties of cohomology systems so as to find the necessary and sufficient conditions that two cohomology systems are isomorphic if their groups are isomorphic. We discovered [5] new numerical invariants called secondary torsions and reached the following result:

THEOREM. *The homotopy type of an A_n^2-polyhedron $(n > 2)$ is determined by its Betti numbers, torsions and secondary torsions.*

In this theorem Betti numbers, torsions and secondary torsions become a *complete* and *independent* system of invariants of the homotopy type of A_n^2-polyhedra.

By an elementary A_n^2-polyhedron we mean one of the following kinds:

(1) $B_1^r = S^r$ $(r = n, n+1, n+2)$;

(2) $B_2(\sigma) = S^n \cup e^{n+1}$, where e^{n+1} is attached to S^n by a map $f: \dot{E}^{n+1} \to S^n$ of degree σ, a power of a prime;

(3) $B_3(\tau) = S^{n+1} \cup e^{n+2}$, where e^{n+2} is attached to S^{n+1} by a map $f: \dot{E}^{n+2} \to S^{n+1}$ of degree τ, a power of a prime;

(4) $B_4 = S^n \cup e^{n+2}$, where e^{n+2} is attached to S^n by an essential map $f: \dot{E}^{n+2} \to S^n$;

(5) $B_5(2^p) = S^n \cup e^{n+1} \cup e^{n+2}$, where e^{n+1} is attached to S^n by an essential map $f: \dot{E}^{n+2} \to S^n$;

(6) $B_6(2^q)=S^n\cup S^{n+1}\cup e^{n+2}$, where $S^n\cap S^{n+1}=x_0$, a point, and e^{n+2} is attached to $S^n\cup S^{n+1}$ by a map $f:\dot{E}^{n+2}\to S^n\cup S^{n+1}$ of the form $a+b$, where a denotes an essential map of $\dot{E}^{n+2}$ onto S^n and b maps $\dot{E}^{n+2}$ onto S^{n+1} with degree 2^q;

(7) $B_7(2^p, 2^q)=B_6(2^q)\cup e^{n+1}$. Attach e^{n+1} to S^n of $B_6(2^q)$ by a map $f:\dot{E}^{n+1}\to S^n$ with degree 2^p.

Take a certain number of elementary polyhedra, choose a point on the sphere of lowest dimension of each elementary polyhedron and identify all these points to a new point p_0, thus forming an A_n^2-polyhedron, K, which is a normal form for the homotopy type of a given A_n^2-polyhedron.

By means of normal A_n^2-polyhedron $\pi_{n+1}(K)$ is computed ([5], [6]), as a generalisation of the well-known Hurewicz theorem. Furthermore, P. J. Hilton [6] computed the $(n+2)$-dimensional homotopy group of A_n^2-polyhedron (if $n\geqslant 3$) while the Borsuk-Spanier cohomotopy group $\pi^n(K^{n+1})$, $(n>3)$, K^{n+1} being a given $(n+1)$-dimensional polyhedron, is expressed [5] by means of the Betti numbers, torsions and secondary torsions of a special A_n^2-polyhedron obtained from K^{n+1} by identifying its $(n-1)$-skeleton to a point.

In the definition of the cohomology ring the Pontrjagin square is involved in place of the Steenrod square. The algebraic classification of cohomology rings seems to be very difficult.

In 1950, J. H. C. Whitehead and myself [7] extended the secondary torsions associated with the A_n^2-polyhedron $(n\geqslant 3)$ to block invariants associated with a finite polyhedron. We [7] considered (μ,Δ,γ)-systems which consist of the whole family of groups $H^n(m)$ $(m=0,2)$ related by the homomorphisms μ,Δ,γ, where $\gamma=\gamma_k^n:H^n(2)\to H^{n+k}(2)$ is supposed to be defined for every even $k>0$ and every $n\geqslant k$. To a given topological space a (μ,Δ,γ)-system is evidently determined by the geometrical method. Since a homotopy equivalence $f:X\to Y$ induces an isomorphism of (μ,Δ,γ)-systems related to Y and X, algebraic invariants of the isomorphism class of (μ,Δ,γ)-systems must be invariants of the homotopy type. From this view-point many numerical homotopy invariants may be found if we are able to classify (μ,Δ,γ)-systems according to their isomorphism classes.

No doubt we may have an algebraic structure if we have a cohomology operation (or a set of cohomology operations) which commutes with the homomorphism between cohomology groups induced by a continuous mapping. Particularly, we take two Steenrod homomorphisms, $\gamma_j^m:H^m(2)\to H^{m+j}(2)$, $\gamma_k^n:H^n(2)\to H^{n+k}(2)$, and construct a special (μ,Δ,γ)-system containing γ_j^m, γ_k^n and their related cohomology groups H^r $(r=m, m+1, m+j, m+j+1, n, n+1, n+k, n+k+1)$ and $H^s(2)$ $(s=m, m+j, n, n+k)$. In [7] it has been actually remarked that block invariants together with Betti numbers and torsions are not enough to characterise isomorphism classes of these special (μ,Δ,γ)-systems, if among the sets of groups

$(H^m, H^{m+1}, H^{m+j}, H^{m+j+1})$ and $(H^n, H^{n+1}, H^{n+k}, H^{n+k+1})$ there are common groups. Now there are two extremities: In the simplest case there is one common group between the sets $(H^m, H^{m+1}, H^{m+j}, H^{m+j+1})$ and $(H^n, H^{n+1}, H^{n+k}, H^{n+k+1})$, but in the most complicated case there exist three common groups. The isomorphism class of (μ,Δ,γ)-systems of the first case has been studied in [8]; block invariants, relative block invariants, Betti numbers and torsions are complete and independent sets of invariants. In the latter case we have $j=k=2$ and $n=m+1$, which system plays an important role in the homotopy type of A_n^3 $(n\geqslant 3)$ polyhedron and is called the A_n^3-system. In a recent paper [9] we discover new numerical invariants called characteristic coefficients and characteristic polynomials and have proved that isomorphism classes of A_n^3-systems are characterised by Betti numbers, torsions, block invariants, relative block invariants, characteristic coefficients and characteristic polynomials. All of these invariants are invariants of a given finite polyhedron.

In the end I remark that general steps to characterise (μ,Δ,γ)-systems are indicated in [8]. We expect to find complete and independent systems of invariants of homotopy types of polyhedra and determine normal forms of these types. Normal forms of polyhedra appear to be useful in several occasions.

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MATHÉMATIQUE

Sur la division des corps matériels en parties

par

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Présenté le 19 Octobre 1956

Un corps Q est, par définition, une répartition de matière dans l'espace, donnée par une fonction $f(P)$; on appelle cette fonction la *densité* du corps en question; elle est définie pour tous les points P de l'espace; elle est non-négative et mesurable. On suppose que *l'ensemble caractéristique* du corps $E=\sum_P \{f(P)>0\}$ est borné et de mesure positive; on suppose aussi que l'intégrale de $f(P)$ sur E est finie: c'est la *masse* du corps Q. On considère comme identiques deux corps dont les densités sont égales à un ensemble de mesure nulle près.

En décomposant l'ensemble caractéristique d'un corps Q en n sous-ensembles E_i $(i=1,2,\ldots,n)$ de mesures positives, on obtient une *division* du corps en question en n *corps partiels*; leurs ensembles caractéristiques respectifs sont les E_i et leurs densités sont définies par les valeurs que prend la densité du corps Q dans ces *ensembles partiels*. En désignant les corps partiels par Q_i, on écrira $Q=Q_1+Q_2+\ldots+Q_n$. Quand on donne d'abord n corps Q_i, dont les ensembles caractéristiques sont disjoints deux à deux à la mesure nulle près, il existe évidemment un corps Q ayant ces Q_i comme autant de parties; on écrira $Q_1+Q_2+\ldots+Q_n=Q$. Ces remarques suffisent pour expliquer la division et la composition des corps.

Le PROBLÈME de cette Note est la division d'un corps en n parties K_i $(i=1,2,\ldots,n)$ et le choix de n points A_i de manière à rendre aussi petite que possible la somme

$$S(K,A)=\sum_{i=1}^{n} I(K_i,A_i) \qquad (K\equiv\{K_i\}, \quad A\equiv\{A_i\}), \tag{1}$$

où $I(Q,P)$ désigne, en général, le *moment d'inertie* d'un corps quelconque Q par rapport à un point quelconque P. Pour traiter ce problème élémentaire nous aurons recours aux lemmes suivants:

a) Q étant donné, $I(Q,P)$ atteint un minimum parfait quand P devient identique avec le centroïde de Q.

b) Si (K,A) est la solution du problème, tout A_i est le centroïde de K_i $(i=1,2,\ldots,n)$.

c) Soient K_1 et K_2 deux corps partiels de Q, obtenus en coupant l'ensemble caractéristique E de Q en deux par un plan; soient A_1 et A_2 les centroïdes respectifs de K_1 et K_2; on aura

$$S(K,A) < I(Q,P)$$

quel que soit le point P.

d) Si (K,A) est la solution du problème, on a $A_i \neq A_j$ pour $i \neq j$ $(i,j=1,2,\ldots,n)$.

e) Soit $\bar{D}$ le plus petit domaine convexe et fermé contenant l'ensemble caractéristique E de Q, et soit P' le point de $\bar{D}$ le plus proche de P; on aura $I(Q,P) \geqslant I(Q,P')$.

Le lemme a) résoud le problème pour $n=1$; il est connu universellement; nous y parlons de minimum *parfait*, car il n'y a pas d'autres points donnant des valeurs extrêmes à I. Le lemme b) résulte de a). Le lemme c) résulte de ce que $I(Q,P)=I(K_1,P)+I(K_2,P)$, de a) et du fait que le centroïde d'un corps Q quelconque est toujours intérieur au domaine $D=\bar{D}-F$ (on a défini $\bar{D}$ dans e) et F est la frontière de $\bar{D}$); on applique ce fait aux corps A_1 et A_2. Le lemme d) résulte de l'application de c) au corps K_i+K_j. Le lemme e) est fondé sur l'inégalité $P'T \leqslant PT$ pour $T \in \bar{D}$.

Soit $A_i \neq A_j$. Le lieu géométrique des points équidistants de A_i et A_j est un plan qui divise l'espace en deux domaines, dont celui contenant A_i est appelé F_{ij}. Le produit $C_i=D\prod_{j\neq i} F_{ij}$ est un domaine borné et convexe, contenu dans D; $D=\bar{D}-F$ (comme ci-dessus) et $\bar{D}$ est l'ensemble dont parle le lemme e).

f) Soit (K,A) la solution du problème. Nous disons que K est la décomposition de Q fournie par $E_i'=C_iE$, E étant l'ensemble caractéristique de Q et C_i les ensembles dont parle le lemme e).

En effet, pour une décomposition quelconque E_i de E on obtient

$$S(K,A)=\iiint_E f(P)k^2(P)\,dv, \qquad (dv=dx\,dy\,dz),$$

où $k(P)=PA_i$ pour $P \in E_i$ $(i=1,2,\ldots,n)$. Il est évident que l'on a toujours

$$k(P) \geqslant h(P)=\min(PA_1,PA_2,\ldots,PA_n)$$

et que, par conséquent, la valeur minimum de $S(K,A)$, pour un A donné, est obtenue lorsque $k(P)=h(P)$ presque partout; or, ce cas n'est réalisé que par la *décomposition spéciale* $\{E_i\}$ définie par les plans équidistants.

Les lemmes b), d) et f) montrent que la solution du problème ne peut être obtenue qu'en réalisant les conditions que l'on ait exactement n points A_i distincts, qu'ils soient les centroïdes des corps partiels K_i et que ces corps soient séparés deux à deux par les plans équidistants relatifs à leurs centroïdes respectifs.

Nous allons établir maintenant l'existence d'une solution, en suivant une voie directe.

Soit m la limite inférieure de $S(X, Y)$ pour tous les (X, Y) possibles; on aura, pour une suite convenable (X^r, Y^r),

$$\lim_{r\to\infty} S(X^r, Y^r) = m . \tag{2}$$

Cette relation subsiste — à cause du lemme d) — lorsqu'on remplace chaque point Y_i^r par le point qui lui est le plus proche parmi les points de $\bar{D}$; on peut donc supposer que tous les Y_i^r dans (2) appartiennent à $\bar{D}$. Il s'ensuit que l'on peut extraire de $\{Y^r\}$ une suite convergente vers Y^0: on entend par là $\lim_{r\to\infty} Y_i^r = Y_i^0$ $(i=1,2,\ldots,n)$ pour la suite partielle (dont les termes sont désignés ici par les mêmes lettres que ceux de la suite primitive). On en tire

$$\lim_{r\to\infty} S(X^r, Y^0) = m \tag{3}$$

pour une certaine suite $\{X^r\}$. Or, il est possible que les n points Y_i^0 ne soient pas tous distincts; soit par exemple $Y_1^0 = Y_2^0$. On aura alors

$$I(X_1^r, Y_1^0) + I(X_2^r, Y_2^0) = I(X_1^r + X_2^r, Y_1^0) . \tag{4}$$

$X_1^r + X_2^r$ est un nouveau corps partiel qui remplace dans S deux corps de la division primitive; ce changement n'altère pas la valeur de S à cause de (4). En poursuivant cette réduction de la somme S on aboutit à une expression (X^r, Y^0) avec s termes Y_i^0 distincts $(i=1,2,\ldots s \leqslant n)$ et la formule (3) subsiste pour l'expression nouvelle. Construisons maintenant la division spéciale relative à Y_i^0 $(i=1,2,\ldots,s)$ (cf. lemme f) (cette division se réduit à $X_1^0 = 0$ dans le cas exceptionnel $s=1$). Cette division X^0 ne dépend pas de r et on obtient

$$S(X^0, Y^0) \geqslant S(X^r, Y^0) . \tag{5}$$

(3) et (5) donnent

$$S(X^0, Y^0) = m . \tag{6}$$

Le nombre des corps partiels dans X^0 est $s \leqslant n$; or, l'inégalité $s < n$ est incompatible avec (6) d'après le lemme d); on voit donc que $s = n$ (X^0, Y^0) est bien la solution du problème principal de cette Note. Ce résultat démontre la possibilité de satisfaire simultanément aux conditions nécessaires, formulées à la fin du paragraphe 1. Pour un corps Q donné, le minimum m est une fonction d'une seule variable n; l'égalité $s = n$

montre que cette fonction est décroissante; il est aussi facile à voir que l'on a $\lim_{n\to\infty} m(n)=0$.

La solution du problème, Q et n étant donnés, est en général unique, mais il y a des corps avec une infinité de solutions: la sphère homogène en est un pour tous les n. Bien entendu, il y a des corps avec un nombre fini de solutions différentes: un cube homogène, par exemple, en a trois pour $n=2$.

Même s'il n'y a qu'une seule solution, les conditions nécessaires du paragraphe 1 ne sont pas suffisantes: un bloc homogène $|x|\leqslant a$, $|y|\leqslant b$, $|z|\leqslant c$ avec $a>b>c$ fournit un exemple pour $n=2$; en effet, en le coupant par le plan $x=0$ en deux et en posant $A_1=(-a/2,0,0)$, $A_2=(a/2,0,0)$, on obtient la solution unique, mais on peut couper le bloc par le plan $y=0$ ou par le plan $x=0$ pour obtenir deux autres divisions qui satisfont aux conditions nécessaires sans toutefois fournir le minimum.

Dans les applications il n'y aura pour la plupart qu'un seul (K,A) satisfaisant aux conditions nécessaires; il paraît que dans ce cas la solution peut être trouvée en partant d'une décomposition K^1 arbitraire en n parties, en définissant A_i^r $(i=1,2,\ldots n)$ comme centroïde de K_i^r, et K^{r+1} comme la décomposition spéciale relative à A^r, pour tous les r naturels; or, il nous manque une démonstration de la convergence de (K^r,A^r) pour $r\to\infty$ vers la solution cherchée.

La question se pose, si l'existence d'une infinité de solutions pour chaque $n(\geqslant 2)$ implique que Q soit un corps de révolution. Une autre question: si l'on a pour un Q donné plusieurs solutions pour certains n, l'ensemble de ces n est-il nécessairement infini?

Diverses questions, par exemple celles des types en anthropologie, ou bien d'autres, d'ordre pratique, comme celles de la normalisation des objets industriels, exigent pour leur solution la détermination de n représentants fictifs d'une nombreuse population, choisis de manière à réduire autant que possible les écarts entre les éléments de la population et ceux de l'échantillon, l'écart étant mesuré entre tout élément réel et l'élément fictif qui lui est le plus proche — voilà les considérations qui ont conduit l'auteur à étudier le cas spécial traité dans cette Note.

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THEORETICAL PHYSICS

The Calculation of the Matrix Components of Energy for Hexagonal Close-Packed Structure

by

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The tight binding method originally proposed by Bloch [1] and worked out in detail by Slater and Koster [2], was used here to investigate the hexagonal close-packed structure.

It is known that this method in the approximation proposed in [2] gives satisfactory quantitative results, if applied to metals in which the electrons responsible for conduction are tightly bound. In particular, it shows correctly all the symmetry properties in energy bands.

Such metals are the transition metals Fe, Co and Ni, which have the $3d$ shell partly and the $4s$ shell completely filled. Fletcher and Wohlfarth [3] and Fletcher [4] applied the tight binding method to β-Ni, which has a face-centered cubic structure.

There is, however, a form of α-Co and α-Ni, which has a hexagonal close-packed structure, and the calculations reported below were performed in order to use them later to study the properties of the energy bands of these metals.

The matrix components of energy between the Bloch sums were calculated using first the general energy integrals (E-integrals) and subsequently the two-centre integrals. The general formula for the matrix component of energy is given by

$$H_{mn}^{\omega\omega'} = (m/n)_{\omega\omega'} = \exp\left[i\mathbf{k}(\mathbf{t}_\omega - \mathbf{t}_{\omega'})\right] \sum_i \exp\left(i\mathbf{k}\mathbf{r}_i\right) \int \varphi_m^*(\mathbf{r} - \mathbf{t}_{\omega'}) H \varphi_n(\mathbf{r} - \mathbf{r}_i - \mathbf{t}_\omega)\, d\mathbf{r},$$

where m and n denote the electronic states; in our case they are the s and d states. $\mathbf{t}_\omega$ denotes the basis vectors. $\varphi_m(\mathbf{r})$ is the eigenfunction of the electrons in an isolated atom. Energy integrals (E-integrals) have the form

$$E_{mn}(\mathbf{t}_{\omega'}, \mathbf{r}_i + \mathbf{r}_\omega) = \int \varphi_m^*(\mathbf{r} - \mathbf{t}_{\omega'})\, H \varphi_n(\mathbf{r} - \mathbf{r}_i - \mathbf{t}_\omega)\, d\mathbf{r}.$$

The hexagonal close-packed lattice can be regarded as the simple hexagonal lattice with two atoms in the unit cell. The translation vectors of hexagonal lattice in a rectangular co-ordinate system are: $\mathbf{A}_1 = (a/2, -\sqrt{3}a/2, 0)$, $\mathbf{A}_2 = (a/2, \sqrt{3}a/2, 0)$, $\mathbf{A}_3 = (0,0,c)$. The minimum distance in simple hexagonal lattice is a (lattice constant). Basis vectors are given by $\mathbf{t}_1 = (0,0,0)$, $\mathbf{t}_2 = (a/2, \sqrt{3}a/6, c/2)$. The lattice obtained by starting from the central atom in the position $(0,0,0)$ is denoted by the index 1, and the lattice obtained by a translation in the position $(a/2, \sqrt{3}a/6, c/2)$ is denoted by 2. In the calculations we used a model of the hexagonal ideal close-packed lattice, i. e. we assumed $|\mathbf{t}_2| = a$. In this case $c/a = 1.633$. The assumption $|\mathbf{t}_2| = a$ is satisfactory for α-Co and α-Ni, because for Co the ratio c/a has the value 1.62 and for Ni $c/a = 1.64$. It is now convenient to use different length units in different directions of the axes of rectangular co-ordinate systems. So we take $\alpha = a/2$, $\beta = \sqrt{3}a/2$, $\gamma = c/2$ in the x,y,z directions respectively.

In the formula for $(m/n)_{\omega\omega'}$ we considered only the integrals representing the interaction between nearest neighbours. Regarding an atom in the position $(0,0,0)$ we have six neighbours of the lattice 1, which are all in the same plane together with the central atom. Their positions in our rectangular co-ordinate system are $(1,-1,0)$, $(2,0,0)$, $(1,1,0)$, $(-1,1,0)$, $(-2,0,0)$, $(-1,-1,0)$. The matrix components of energy are of the type $(m/n)_{11}$. We also have six neighbours belonging to the lattice 2, which are placed at a distance $c/2$ above and below this plane. Their positions are $(1,1/3,1)$, $(-1,1/3,1)$, $(0,-2/3,1)$, $(1,1/3,-1)$, $(-1,1/3,-1)$, $(0,-2/3,-1)$. The matrix components of energy are here of the $(m/n)_{12}$ type. Accordingly, the sum for $(m/n)_{\omega\omega'}$ will contain six terms. $(m/n)_{11}$ also contains the term with $\mathbf{r}_i = (0,0,0)$.

Since we consider six states (five d and one s states) and in the unit cell we have two atoms, the general matrix of energy has $12 \times 12 = 144$ elements. Using Hermitian and symmetry properties of the Hamiltonian and the symmetry properties of the eigenfunctions of the isolated atoms we find that the matrix of energy has only 42 different components. Other components are either equal or conjugate to these. The symmetry properties of the Hamiltonian and of the eigenfunctions make it possible to reduce still further the number of different E-integrals which occur in the matrix components of energy.

In Table I we have given the matrix components of energy in terms of E-integrals. The abbreviation $\xi = ak_x/2$, $\eta = \sqrt{3}ak_y/2$, $\zeta = ck_z/2$ has been used in this table. Since in many matrix components we have the same dependence on ξ,η,ζ, we have written only one element of this type and on the right hand side of the table the components with the same dependence on $\mathbf{k}$ are given. Evidently they differ only in the form of E-integrals.

Table I

$(s/s)_{11}$ | $(s/3z^2-r^2)_{11}$

$E_{s,s}(0,0,0)+2E_{s,s}(1,-1,0)\,(2\cos\xi\cos\eta+\cos 2\xi)$ | $(3z^2-r^2/3z^2-r^2)_{11}$

$(s/s)_{12}$ | $(s/3z^2-r^2)_{12}$

$2E_{s,s}(1,\frac{1}{3},1)\cos\zeta[(2\cos\xi\cos\eta/3+\cos 2\eta/3)+$ | $(3z^2-r^2/3z^2-r^2)_{12}$

$+i(2\cos\xi\sin\eta/3-\sin 2\eta/3)]$

$(s/xy)_{11}$ | $(yz/xz)_{11}$

$2[E_{s,xy}(1,-1,0)-E_{s,xy}(1,1,0)]\sin\xi\sin\eta+$ | $(xy/x^2-y^2)_{11}$

$+2i\{[E_{s,xy}(1,-1,0)+E_{s,xy}(1,1,0)]\sin\xi\cos\eta+$

$+E_{s,xy}(2,0,0)\sin 2\xi\}$ | $(xy/3z^2-r^2)_{11}$

$(s/xy)_{12}$ | $(yz/xz)_{12}$

$-4E_{s,xy}(1,\frac{1}{3},1)\sin\xi\cos\zeta(\sin\eta/3-i\cos\eta/3)$ | $(xy/x^2-y^2)_{12}$

$(xy/3z^2-r^2)_{12}$

$(s/yz)_{11}=(s/xz)_{11}=(xy/yz)_{11}=(xy/xz)_{11}=(yz/x^2-y^2)_{11}=$

$=(yz/3z^2-r^2)_{11}=(xz/x^2-y^2)_{11}=(xz/3z^2-r^2)_{11}=0$

$(s/yz)_{12}$ | $(xy/xz)_{12}$

$2\sin\zeta[-2E_{s,yz}(1,\frac{1}{3},1)\cos\xi\sin\eta/3+$ | $(yz/3z^2-r^2)_{12}$

$+E_{s,yz}(0,-\frac{2}{3},1)\sin 2\eta/3]+2i\sin\zeta[2E_{s,yz}(1,\frac{1}{3},1)\cos\xi\cos\eta/3+$

$+E_{s,yz}(0,-\frac{2}{3},1)\cos 2\eta/3]$ | $(yz/x^2-y^2)_{12}$

$(s/xz)_{12}$ | $(xy/yz)_{12}$

$-4E_{s,xz}(1,\frac{1}{3},1)\sin\xi\sin\zeta(\cos\eta/3+i\sin\eta/3)$ | $(xz/x^2-y^2)_{12}$

$(xz/3z^2-r^2)_{12}$

$(s/x^2-y^2)_{11}$ | $(x^2-y^2/3z^2-r^2)_{11}$

$E_{s,x^2-y^2}(0,0,0)+2[E_{s,x^2-y^2}(1,-1,0)+E_{s,x^2-y^2}(1,1,0)]\cos\xi\cos\eta+$

$+2E_{s,x^2-y^2}(2,0,0)\cos 2\xi+2i[E_{s,x^2-y^2}(1,1,0)-$

$-E_{s,x^2-y^2}(1,-1,0)]\cos\xi\sin\eta$

$(s/x^2-y^2)_{12}$ | $(xy/xy)_{12}$

$2\cos\zeta[2E_{s,x^2-y^2}(1,\frac{1}{3},1)\cos\xi\cos\eta/3+$ | $(yz/yz)_{12}$

$+E_{s,x^2-y^2}(0,\frac{2}{3},1)\cos 2\eta/3]+$ | $(xz/xz)_{12}$

$+2i\cos\zeta[2E_{s,x^2-y^2}(1,\frac{1}{3},1)\cos\xi\sin\eta/3-$ | $(x^2-y^2/x^2-y^2)_{12}$

$-E_{s,x^2-y^2}(0,-\frac{2}{3},1)\sin 2\eta/3]$ | $(x^2-y^2/3z^2-r^2)_{12}$

$(xy/xy)_{11}$ | $(yz/yz)_{11}$

$E_{xy,xy}(0,0,0)+4E_{xy,xy}(1,-1,0)\cos\xi\cos\eta+$ | $(xz/xz)_{11}$

$+2E_{xy,xy}(2,0,0)\cos 2\xi$ | $(x^2-y^2/x^2-y^2)_{11}$.

We have here 72 different E-integrals, the calculation of which would be very laborious. Therefore it is convenient to use the two-centre approximation. To express the E-integrals in terms of the two-centre integrals $(ss\sigma)$, $(sd\sigma)$, $(dd\sigma)$, $(dd\pi)$, $(dd\delta)$ we used Table I in paper [2].

The matrix components expressed in terms of the two-centre integrals are given in Table II.

Table II

$(s/s)_{11}$	$s_0 + 2(ss\sigma)_1(2\cos\xi\cos\eta + \cos 2\xi)$
$(s/s)_{12}$	$2(ss\sigma)_1\zeta\cos\zeta[(2\cos\xi\cos\eta/3 + \cos 2\eta/3) +$ $+ i(2\cos\xi\sin\eta/3 - \sin 2\eta/3)]$
$(s/xy)_{11}$	$-3(sd\sigma)_1\sin\xi\sin\eta$
$(s/xy)_{12}$	$-(sd\sigma)_1\sin\xi\cos\zeta(\sin\eta/3 - i\cos\eta/3)$
$(s/yz)_{11}$	0
$(s/yz)_{12}$	$-2\sqrt{\frac{2}{3}}(sd\sigma)_1\sin\zeta[(\cos\xi\sin\eta/3 + \sin 2\eta/3) -$ $- i(\cos\xi\cos\eta/3 - \cos 2\eta/3)]$
$(s/xz)_{11}$	0
$(s/xz)_{12}$	$-2\sqrt{2}(sd\sigma)_1\sin\xi\sin\zeta(\cos\eta/3 + i\sin\eta/3)$
$(s/x^2-y^2)_{11}$	$-\sqrt{3}(sd\sigma)_1(\cos\xi\cos\eta - \cos 2\xi)$
$(s/x^2-y^2)_{12}$	$\frac{1}{3}\sqrt{3}(sd_\sigma)_1\cos\zeta[(\cos\xi\cos\eta/3 - \cos 2\eta/3) +$ $+ i(\cos\xi\sin\eta/3 + \sin 2\eta/3)]$
$(s/3z^2-r^2)_{11}$	$-(sd\sigma)_1(2\cos\xi\cos\eta + \cos 2\xi)$
$(s/3z^2-r^2)_{12}$	$(sd\sigma)_1\cos\zeta[(2\cos\xi\cos\eta/3 + \cos 2\eta/3) +$ $+ i(2\cos\xi\sin\eta/3 - \sin 2\eta/3)]$
$(xy/xy)_{11}$	$d_0 + 2(dd\pi)_1\cos 2\xi + [\frac{9}{4}(dd\sigma)_1 + (dd\pi)_1 + \frac{3}{4}(dd\delta)_1]\cos\xi\cos\eta$
$(xy/xy)_{12}$	$2\cos\zeta\{\frac{1}{3}[(dd\pi)_1 + 2(dd\delta)_1]\cos 2\eta/3 +$ $+ \frac{1}{2}[\frac{1}{4}(dd\sigma)_1 + (dd\pi)_1 + \frac{1}{4}^1(dd\delta)_1]\cos\xi\cos\eta/3\} +$ $2i\cos\zeta\{-\frac{1}{3}[(dd\pi)_1 + 2(dd\delta)_1]\sin 2\eta/3 +$ $+ \frac{1}{2}[\frac{1}{4}(dd\sigma)_1 + (dd\pi)_1 + \frac{1}{4}^1(dd\delta)_1]\cos\xi\sin\eta/3\}$
$(xy/xy)_{11}$	0
$(xy/yz)_{12}$	$-\sqrt{\frac{2}{3}}[\frac{1}{2}(dd\sigma)_1 + \frac{4}{3}(dd\pi)_1 - \frac{1}{6}^1(dd\delta)_1]\times$ $\times\sin\xi\sin\zeta(\cos\eta/3 + i\sin\eta/3)$
$(xy/xz)_{11}$	0
$(xy/xz)_{12}$	$2\sqrt{2}\sin\zeta\{\frac{1}{4}[-(dd\sigma)_1 + (dd\delta)_1]\cos\xi\sin\eta/3 +$ $+ \frac{1}{3}[-(dd\pi)_1 + (dd\delta)_1]\sin 2\eta/3\} +$ $+ 2\sqrt{2}\,i\sin\zeta\{\frac{1}{4}[(dd\sigma)_1 - (dd\delta)_1]\cos\xi\cos\eta/3 +$ $+ \frac{1}{3}[-(dd\pi)_1 + (dd\delta)_1]\cos 2\eta/3\}$
$(xy/x^2-y^2)_{11}$	$\sqrt{3}[\frac{3}{4}(dd\sigma)_1 - (dd\pi)_1 + \frac{1}{4}(dd\delta)_1]\sin\xi\sin\eta -$
$(xy/x^2-y^2)_{12}$	$-\frac{1}{3}\sqrt{3}[\frac{1}{4}(dd\sigma)_1 - \frac{1}{3}(dd\pi)_1 + \frac{1}{12}(dd\delta)_1]\times$ $\times\sin\xi\cos\zeta(\sin\eta/3 - i\cos\eta/3)$
$(xy/3z^2-r^2)_{11}$	$\frac{3}{2}[(dd\sigma)_1 - (dd\delta)_1]\sin\xi\sin\eta -$
$(xy/3z^2-r^2)_{12}$	$-[\frac{1}{2}(dd\sigma)_1 - \frac{4}{3}(dd\pi)_1 + \frac{5}{6}(dd\delta)_1]\times$ $\times\sin\xi\cos\zeta(\sin\eta/3 - i\cos\eta/3)$
$(yz/yz)_{11}$	$d_0 + [3(dd\pi)_1 + (dd\delta)_1]\cos\xi\cos\eta + 2(dd\delta)_1\cos 2\xi$
$(yz/yz)_{12}$	$\frac{2}{3}\cos\zeta\{[2(dd\sigma)_1 + \frac{1}{3}(dd\pi)_1 + \frac{2}{3}(dd\delta)_1]\cos 2\eta/3 +$ $+ [(dd\sigma)_1 + \frac{9}{6}(dd\pi)_1 + \frac{1}{6}^1(dd\delta)_1]\cos\xi\cos\eta/3\} +$ $+ \frac{2}{3}i\cos\zeta\{-[2(dd\sigma)_1 + \frac{1}{3}(dd\pi)_1 + \frac{2}{3}(dd\delta)_1\sin 2\eta/3 +$ $+ [(dd\sigma)_1 + \frac{9}{6}(dd\pi)_1 + \frac{1}{6}^1(dd\delta)_1]\cos\xi\sin\eta/3\}$
$(yz/xz)_{11}$	$\sqrt{3}[-(dd\pi)_1 + (dd\delta)_1]\sin\xi\sin\eta$
$(yz/xz)_{12}$	$-\frac{2}{3}\sqrt{3}[(dd\sigma)_1 - \frac{5}{6}(dd\pi)_1 - \frac{1}{6}(dd\delta)_1]\times$ $\times\sin\xi\cos\zeta(\sin\eta/3 - i\cos\eta/3)$

$(yz/x^2-y^2)_{11}$ 0

$(yz/x^2-y^2)_{12}$ $\frac{2}{3}\sqrt{2}\sin\zeta\{[\frac{1}{2}(dd\sigma)_1+\frac{1}{3}(dd\pi)_1-\frac{5}{6}(dd\delta)_1]\sin 2\eta/3+$
$+[-\frac{1}{4}(dd\sigma)_1+\frac{4}{3}(dd\pi)_1-\frac{1}{1}\frac{3}{2}(dd\delta)_1]\cos\xi\sin\eta/3\}+$
$+\frac{2}{3}\sqrt{2}\,i\sin\zeta\{[\frac{1}{2}(dd\sigma)_1+\frac{1}{3}(dd\pi)_1-\frac{5}{6}(dd\delta)_1]\cos 2\eta/3+$
$+[\frac{1}{4}(dd\sigma)_1-\frac{4}{3}(dd\pi)_1+\frac{1}{1}\frac{3}{2}(dd\delta)_1]\cos\xi\cos\eta/3\}$

$(yz/3z^2-r^2)_{11}$ 0

$(yz/3z^2-r^2)_{12}$ $-\frac{2}{3}\sqrt{2}[\frac{1}{2}(dd\sigma)_1-\frac{1}{3}(dd\pi)_1-\frac{1}{6}(dd\delta)_1]\sin\zeta\times$
$\times[(\cos\xi\sin\eta/3+\sin 2\eta/3)-i(\cos\xi\cos\eta/3-\cos 2\eta/3)]$

$(xz/xz)_{11}$ $d_0+[(dd\pi)_1+3(dd\delta)_1]\cos\xi\cos\eta+2(dd\pi)_1\cos 2\xi$

$(xz/xz)_{12}$ $2\cos\zeta\{\frac{1}{3}[2(dd\pi)_1+(dd\delta)_1]\cos 2\eta/3+$
$+[(dd\sigma)_1+\frac{1}{2}(dd\pi)_1+\frac{1}{2}(dd\delta)_1]\cos\xi\cos\eta/3\}+$
$+2i\cos\zeta\{-\frac{1}{3}[2(dd\pi)_1+(dd\delta)_1]\sin 2\eta/3+$
$+[(dd\sigma)_1+\frac{1}{2}(dd\pi)_1+\frac{1}{2}(dd\delta)_1]\cos\xi\sin\eta/3\}$

$(xz/x^2-y^2)_{11}$ 0

$(xz/x^2-y^2)_{12}$ $-\sqrt{\frac{2}{3}}[\frac{1}{2}(dd\sigma)_1+\frac{4}{3}(dd\pi)_1-\frac{1}{6}(dd\delta)_1]\times$
$\times\sin\xi\sin\zeta(\cos\eta/3+i\sin\eta/3)$

$(xz/3z^2-r^2)_{11}$ 0

$(xz/3z^2-r^2)_{12}$ $-\sqrt{2}[(dd\sigma)_1-\frac{2}{3}(dd\pi)_1-\frac{1}{3}(dd\delta)_1]\times$
$\times\sin\xi\sin\zeta(\cos\eta/3+i\sin\eta/3)$

$(x^2-y^2/x^2-y^2)_{11}$ $d_0+[\frac{3}{4}(dd\sigma)_1+3(dd\pi)_1+\frac{1}{4}(dd\delta)_1]\cos\xi\cos\eta+$
$+\frac{1}{2}[3(dd\sigma)_1+(dd\delta)_1]\cos 2\xi$

$(x^2-y^2/x^2-y^2)_{12}$ $\frac{2}{3}\cos\zeta\{[\frac{1}{4}(dd\sigma)_1+\frac{2}{3}(dd\pi)_1+\frac{2}{1}\frac{5}{2}(dd\delta)_1]\cos 2\eta/3+$
$+\frac{1}{2}[\frac{1}{4}(dd\sigma)_1+\frac{1}{3}\frac{1}{}(dd\pi)_1+\frac{9}{1}\frac{7}{2}(dd\delta)_1]\cos\xi\cos\eta/3\}+$
$+\frac{2}{3}i\cos\zeta\{-[\frac{1}{4}(dd\sigma)_1+\frac{2}{3}(dd\pi)_1+\frac{2}{1}\frac{5}{2}(dd\delta)_1]\sin 2\eta/3+$
$+\frac{1}{2}[\frac{1}{4}(dd\sigma)_1+\frac{1}{3}\frac{1}{}(dd\pi)_1+\frac{9}{1}\frac{7}{2}(dd\delta)_1]\cos\xi\sin\eta/3\}$

$(x^2-y^2/3z^2-r^2)_{11}$ $\frac{1}{2}\sqrt{3}[(dd\sigma)_1-(dd\delta)_1](\cos\xi\cos\eta-\cos 2\xi)$

$(x^2-y^2/3z^2-r^2)_{12}$ $\frac{2}{3}\sqrt{3}\cos\zeta\{[-\frac{1}{4}(dd\sigma)_1+\frac{2}{3}(dd\pi)_1]-\frac{5}{1}\frac{}{2}(dd\delta)_1]\cos 2\eta/3+$
$+\frac{1}{4}[(dd\sigma)_1-\frac{2}{3}(dd\pi)_1+\frac{5}{1}\frac{}{2}(dd\delta)_1]\cos\xi\cos\eta/3\}+$
$+\frac{2}{3}\sqrt{3}\,i\cos\zeta\{-[-\frac{1}{4}(dd\sigma)_1+\frac{2}{3}(dd\pi)_1-\frac{5}{1}\frac{}{2}(dd\delta)_1]\sin 2\eta/3+$
$+[\frac{1}{4}(dd\sigma)_1-\frac{2}{3}(dd\pi)_1+\frac{5}{1}\frac{}{2}(dd\delta)_1]\cos\xi\sin\eta/3\}$

$(3z^2-r^2/3z^2-r^2)_{11}$ $d_0+\frac{1}{2}[(dd\sigma)_1+3(dd\delta)_1](2\cos\xi\cos\eta+\cos 2\xi)$

$(3z^2-r^2/3z^2-r^2)_{12}$ $[\frac{1}{2}(dd\sigma)_1+\frac{4}{3}(dd\pi)_1+\frac{1}{6}(dd\delta)_1]\cos\zeta\times$
$\times[(2\cos\xi\cos\eta/3+\cos 2\eta/3)+i(2\cos\xi\sin\eta/3-\sin 2\eta/3)]$

It may be seen from the above that the two-centre approximation considerably simplifies the calculations. Instead of the 72 E-integrals we now have only 7 integrals, s_0, d_0, $(ss\sigma)_1$, $(sd\sigma)_1$, $(dd\sigma)_1$, $(dd\pi)_1$ and $(dd\delta)_1$. When we know the **k** dependence of the matrix components and

the values of the two-centre integrals, the symmetry properties of the energy bands can be studied.

I wish to thank Dr M. Suffczyński for his great interest in this work and for valuable discussions.

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EXPERIMENTAL PHYSICS

Investigation of an Electromagnetic Cascade of Very High Energy in the First Stage of Its Development in Nuclear Emulsions

by

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Presented by H. NIEWODNICZAŃSKI on September 18, 1956

Information on some examples of high energy showers of electron pairs has recently been published. The development of some of these showers seems to show that they may be initiated by several photons [1]-[5]. At the same time the range of energy, in which electron showers initiated by a single photon have been found and investigated in emulsions, has been extended to above 10^{11} *eV* [4], [6], [7].

One of the anomalies found in high energy showers is the deficiency of low energy pairs as compared with the number of high energy pairs. This effect has been reported for showers assumed to be initiated by several photons by Debenedetti et al. [2], and for a shower probably initiated by a single photon, by the authors of the present paper [6]. It was suggested by Wataghin [8] that these anomalies have a general character for all electronic showers of high energy ($\simeq 10^{12}$ *eV*). Dyson [9] suggested that this anomaly might be explained on the basis of the theories of Ter Mikaelian [10] and Landau and Pomerančuk [11]. It is very important in this connection to determine whether the anomaly really exists in the showers initiated by a single photon of very high energy. It therefore seems very desirable to carry out investigations on cascades deriving from single photons of the highest energies at their beginning. At greater depths these anomalies should disappear because of the decrease in the energy of the electrons of the cascade.

Hitherto there were known in the literature only two cascades, generated by single photons of energies of $\simeq 10^{12}$ *eV*. These were recently analysed by Pinkau [7].

The present paper is intended to give an account of an analysis of a cascade generated probably by a single photon of an energy approaching the value of 10^{12} *eV*, particular consideration being given to the beginning

of the development of the cascade where we could expect to find such an anomaly. Preliminary results of the measurements of this cascade have already been published [6].

The shower consists of high energy pairs, 14 of which are generated within 1.55 rad. length from the origin of the first pair. Most of these pairs are included within a very narrow cone of an angle of about 10^{-4} radians. The length of the cascade in one emulsion is about 4.2 mm. The data on the observed pairs are given in Table I. Most of the pairs are apparent tridents, as can be seen from column 7 of Table I.

The evaluation of energy of the primary photon initiating the cascade was carried out with the energy spectrum of electrons at a depth of 2.5 rad. length. The scattering measurements were made on the tracks contained within a circle of a radius of 250 μ from the core. The number of tracks of electrons with energies higher than 5.10^8 eV within the circle of a radius of 200 μ was 34. The calculations of the full number of electrons in this energy interval at this depth, on the basis of the lateral distribution of particles, were carried out by a method described by Pinkau [7]. Then, using the tables of Janossy and Messel [12], the energy E_0 of the primary photon could be found if we assumed the equipartition of energy for particles of the first pair. From these measurements we obtained $E_0=(7.0^{+3.4}_{-2.6})\times 10^{11}$ eV. The limits of error of the value of E_0 were found, taking Janossy's [13] standard deviations for a given number of tracks and finding the values of energy corresponding to the extreme number of electrons of energies greater than $5\cdot 10^8$ eV. From the value of E_0 the numbers of electrons of different energies for various radii were obtained, and they are in agreement with the observed values within Janossy's standard deviations.

We obtained information on the energy of the primary pair independently in another way, from measurements of ionization on the first part of the unresolved track of the first pair. From these measurements [14]-[16] it was possible with the use of the formula given by Čudakov [14] to estimate the opening angle of the first pair. We obtained the value $\omega=3.10^{-6}$ radians, and hence from the formula $E=4mc^2/\omega$ we obtained for E_0 the value $\sim 10^{12}$ eV. We consider these measurements as only approximate, since in the formula from which we evaluated the angle there are constants which are not accurately known.

We have now investigated the spectrum of electrons at a depth of 1.55 rad. length. In Fig. 1 the integral energy spectrum of electrons observed at this depth is shown. This spectrum is obtained directly from the figures given in Table I, taking into account the energy losses of electrons by "bremsstrahlung" and ionization. The circles show the numbers of electrons with energy greater than the given value. The vertical lines give the uncertainty of energy determination. The full line shows the spectrum of electrons calculated from the cascade theory (Approxi-

mation B) [12] on the assumption that the energy of the primary photon is $E_0 = 7.10^{11}$ *eV* as mentioned above. The dotted lines represent the spectra calculated for energies giving the limits of error of the primary photon energy (4.4 or 10.4×10^{11} *eV*).

As may be seen from Fig. 1 there is a deficiency in the number of electrons of energy lower than 5.10^8 *eV* as compared with the prediction of the cascade theory.

Qualitatively it is possible to explain this effect according to the suggestions of Dyson [9] on the basis of the theory of Ter-Mikaelian [10] and Landau and Pomerančuk [11]. According to these theories, if an

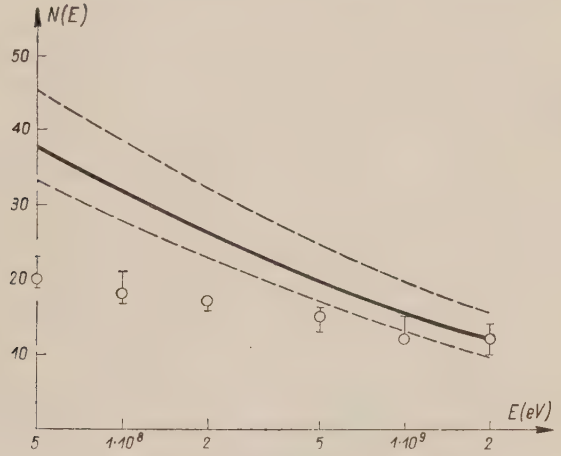

Fig. 1.

electron moves through photographic emulsion with an energy E, greater than $\simeq 10^{10}$ *eV*, the spectrum of "bremsstrahlung" photons radiated by this electron, for photon energies lower than a critical energy k_c, is changed from the Bethe-Heitler form $\left(\sim\frac{dk}{k}\right)$ to the Landau-Pomerančuk form $\left(\sim\frac{dk}{\sqrt{k}}\right)$, and is strongly cut down for low photon energies. For photographic emulsions, $k_c \simeq 8.10^{-15} E^2$. This means that for the two electrons of our first pair the energy of photons below which we might expect a lack of photons is $k_c \simeq 10^9$ *eV*. Since at the depth of $t = 1.55$ rad. length the observed energy spectrum of electrons is strongly influenced by the spectrum of the photons radiated by the first pair, it is possible to explain the observed deficiency of electrons of energies 10^8 *eV* and lower by the lack of photons of these energies in the radiation emitted by the first two electrons. This explanation is supported by direct observation of pairs generated on the tracks of the first pair. It can be seen (Table I) that no photons of energy smaller than 10^9 *eV* were converted on the left track, whereas some pairs with energies $\sim 10^8$ are seen

only on the right track. This might be explained by assuming an asymmetry of energies in the two electrons of the first pair. In consequence of the $k_c \sim E^2$ dependence, k_c may differ for both electrons of the first pair by one order of magnitude.

It seems that the observed deficiency of low energy electrons at the depth $t=1.55$ rad. length is outside the limits of the probable fluctuations. Nevertheless it is not possible to conclude quantitatively from this example whether it is in accordance with the theory. It is thus very desirable to check this effect in other high energy cascades generated by single photons of energy 10^{12} eV or higher.

TABLE I

Pair	Distance from the point of origin of the first pair μ	E_1 eV	E_2 eV	E_1+E_2 eV	Most probable parent pair	Radial distance from the nearest electron track μ
1	0	—	—	7.0×10^{11}	—	—
2	9400	2.0×10^{8}	1.0×10^{8}	3.0×10^{8}	1 (l) or 1 (r) *)	$<0.5_0$
3	16400	1.3×10^{8}	1.0×10^{7}	1.4×10^{8}	1 (r)	$<0.4_5$
4	17500	6.0×10^{8}	$\geqslant7.0\times10^{8}$	$\geqslant1.3\times10^{9}$	1 (l)	$<0.2_6$
5	23800	1.3×10^{8}	8.0×10^{7}	2.1×10^{8}	1 (r)	1.0_8
6	27800	$\geqslant1.0\times10^{9}$	7.5×10^{8}	$\geqslant1.8\times10^{9}$	1 (l)	$<0.2_3$
7	30000	$<6.0\times10^{7}$	6.0×10^{7}	$<1.2\times10^{8}$	?	12.6
8	30600	—	—	$>1.3\times10^{10}$ (a)	1 (l)	$<0.4_5$
9	34900	—	—	5.2×10^{9} (b)	1 (l) or 8	$<0.2_3$
10	38700	1.0×10^{7}	6.8×10^{6}	1.7×10^{7}	6	$<0.4_5$
11	40900	—	—	$>1.0\times10^{10}$ (c)	1 (r)	1.3_1
12	41600	—	—	$>3.9\times10^{10}$ (a)	1 (l)	$<0.8_4$
13	42800	—	—	$>2.6\times10^{10}$ (a)	1 (l) or 12	$<1.3_3$
14	43500	$\geqslant2.7\times10^{8}$	1.0×10^{8}	$\geqslant3.7\times10^{8}$	8	0.9_5

*) — (l) or (r) means left or right track of the pair.

(a) — the lower limit of energy estimated from the opening angle of the core containing several tracks using the formula of Borsellino. It is highly probable that this value is underestimated, since the influence of multiple scattering is neglected.

(b) — from relative scattering measurements on the assumption of equipartition of energy.

(c) — as in (a) — measurements taken between the tracks of this pair.

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EXPERIMENTAL PHYSICS

The Ratio of the Number of Photons to the Number of Electrons in Extensive Air Showers of Cosmic Radiation

by

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Presented by H. NIEWODNICZAŃSKI on September 19, 1956

Recently various authors have investigated the transition curve of extensive air shower particles in lead [1]-[4]. With these measurements is connected the problem of the ratio p/e of the number of photons to the number of electrons in extensive showers.

In the methods of measurement of p/e, in which we cover one or more counter trays with the absorber, we may evaluate from experimental data the quantity

$$R(t)=P_e(t)+\frac{p}{e}\cdot P_p(t)\,, \tag{1}$$

where P_e and P_p are the probabilities that an electron or a photon respectively, falling on the absorber of a given thickness t, will produce beneath the absorber at least one secondary electron, which operates the counter tray. The functions $P_e(t)$ and $P_p(t)$ have been evaluated theoretically by Arley [5], and they are conventionally adopted by most authors (except Millar) considering the problem of the ratio p/e in spite of the objections against Arley's theory. Knowing the values of P_e and P_p, it is possible to evaluate the ratio p/e from formula (1).

In the anti-coincidence method we make use of the counter telescope, in which an absorber is placed between the two trays; then we estimate the rate of events in which only the lower tray of the telescope is operated. The rate of these anti-coincidences depends only on the expression $p/e\cdot P_p$, but does not depend on P_e, and this decides on the superiority of the anti-coincidence method.

In the first series of experiments concerning measurements of p/e, the values obtained were rather low, namely 0.25 [1] and 0.12 and 0.3 [2]. It was difficult to explain, from the point of view of the one-dimensional cascade theory, such a low value of p/e, since it predicts for this ratio

the value $\geqslant 1$. Milone in the last of his papers [3] gives for this ratio the value 0.75 ± 0.20, and Massalski [4], 0.8 and 1.0 ± 0.3.

Apparatus

We used in our experiment a modified version of the apparatus previously employed. The detector of extensive showers was composed of three counter trays A, B, C, each of an area $S = 0.468$ sq. m., placed in the corners of an equilateral triangle with sides of 3.4 m. In the centre of the triangle was placed a telescope composed of three counter trays D, E, F, each of an area $s = r \cdot S = 0.290$ sq. m. Tray E was placed immediately above tray F, whereas between trays D and E it was possible to place an absorber 15 cm. thick. The telescope was enclosed by lead walls 10 cm. thick and a lead base 5 cm. deep. All counters were made of brass tubes with walls 1 mm. thick. The measurements were performed in Cracow at an altitude of 229 m. above sea level.

Principles of measurements and their results

Two series of measurements were performed. In the first series lead absorbers from 0 to 25 cm. thick were placed over the telescope DEF. In the second series lead absorbers 0 to 15 cm. thick were placed between the trays D and E. In each of these series the following were registered: threefold coincidences $(ABC) = T$; fourfold coincidences (TD), (TE), (TF); fivefold coincidences (TDE), (TDF), (TEF); sixfold coincidences $(TDEF)$. In the anti-coincidence method we used an arrangement in which one tray (D) was placed over the absorber, while the second tray (E) was below it. The third tray of the telescope (F) was added to eliminate the influence of the low energy penetrating photons of only several MeV which are present in relatively large numbers beneath thicker lead absorbers, and distinctly contribute to the registered rates of coincidences when below the absorber one counter tray is operated; they do not, however, influence the readings when two trays under the absorber are operated in coincidence [6], [7]. All the coincidences may be divided into two groups: A and B. Group A comprises the measurements of transition curves in which the absorber is placed over the telescope containing one, two or three trays of counters. The rates of coincidences of group A may be expressed by the formula

$$(2) \qquad A = \int_0^\infty K x^{-(\gamma+1)} (1 - e^{-Sx})^3 \left(1 - e^{-(P_e + p/e \cdot P_p + k) r' r \cdot Sx}\right) dx =$$

$$= C \cdot S^\gamma \left\{ W_3 + h \left[\left(P_e + \frac{p}{e} \cdot P_p + k \right) r' r \right] \right\},$$

where x is the density of particles of the shower falling on the absorber,

$W_3=-3+3\cdot 2^\gamma-3^\gamma$, $h(z)=-z^\gamma+3(1+z)^\gamma-3(2+z)^\gamma+(3+z)^\gamma$, $K\cdot x^{-(\gamma+1)}dx$ is the differential spectrum of densities of registered showers, and $r'\cdot r\cdot S$ is the effective area of the telescope applied in measurements.

From the ratio $(TD)/T$ in measurements without absorber we evaluated $\gamma=1.41\pm 0.02$. By means of formula (2) we can find, for all kinds of coincidences, the quantities $R(t)=(P_e+p/e\cdot P_p+k)r'r$, corresponding to different thicknesses of the absorber. From these quantities, after subtracting the penetrating component $k\cdot r'\cdot r$ and normalisation of the curves obtained for thickness of the absorber $t=0$, we evaluate the functions $R(t)=P_e+p/e\cdot P_p$. In the normalisation we must take into account the thicknesses of the counter walls.

In this way we obtain from measurements of the group A the quantities $R_1(t)$, $R_2(t)$ and $R_3(t)$, corresponding to cases when beneath the absorber there are operated one, two or three trays of counters. The quantity $R_1(t)$ has been corrected for contribution of penetrating low energy photons. From the values of R_1, R_2 and R_3, we evaluate by means of the formula (1), the ratio p/e for different thicknesses of the absorber. They are shown in Table I.

We consider a modified anti-coincidence method as being the most convenient.

TABLE I

Values of the ratio p/e evaluated from measurements

with an absorber placed over the telescope, from the functions			with a modified anti-coincidence method from the differences of rates of coincidences for two positions of the absorber: over the telescope, and between its two upper trays		
t mm.	$R_1(t)$	$R_2(t)$	$R_3(t)$	$(TDEF)$	(TDE)	(TDF)
3	0.72	0.72	0.66	0.62	0.50	0.61
5	0.82	0.81	0.83	0.98	0.69	0.89
7	0.78	0.78	0.69	0.80	0.77	0.71
10	0.72	0.71	0.68	0.85	0.65	0.86
17	0.61	0.60	0.50	0.42	0.53	0.57
25	0.71	0.72	0.57	0.47	0.91	0.70

In this method we make use of the differences of rates of corresponding coincidences registered by means of an absorber placed over the telescope (group A), and between its two upper trays (group B). These differences may be expressed by the formula

$$(3) \qquad C_{\text{anti}} = A - B = \int_0^\infty K \cdot x^{-(\gamma+1)} (1 - e^{-Sx})^3 (1 - e^{-p/e \cdot P_p \cdot r' r S x}) e^{-rSx} dx =$$

$$= h\left[r\left(1 + r' \frac{p}{e} \cdot P_p\right)\right] - h(r).$$

Using this formula we can from experimental data immediately evaluate $p/e \cdot P_p$, and, in order to determine the ratio p/e, we require only one theoretical quantity, P_p. The main advantage of this method, as compared with the ordinary anti-coincidence method, is that we do not need here any normalisation of the experimental data. The values of the ratio p/e obtained with the anti-coincidence method are also given in Table I. From this table it is evident that the values of p/e obtained with both methods are concordant within the limits of error.

In connection with these results let us discuss the following remarks. From the fact that the results of measurements of transition curves obtained in arrangements with different distances of registering trays from the absorber have given concordant values of p/e, and from the fact that the latter practically do not depend on the thickness of the absorber, we may conclude that our measurements are not influenced markedly by the scattering of particles in the absorber. From the fact of the independence between the results obtained and the thickness of the absorber, we conclude that the result is not greatly influenced, in our case, by the change of mean density of particles of showers registered by our apparatus, which is the result of the change in the thickness of the absorber. In our case the mean density of the particles is comprised in the limits between 10 and 20 per sq. m.

As mentioned above, it is not quite correct to use the values of P_e and P_p from Arley's theory. In our case we use only one of these functions, namely P_p. But this function does not seem to depend strongly on the assumptions of the theory. In this matter the following consideration may help to give a rough picture. From the position of the maximum of the transition curve we can roughly estimate that the main contribution to registering coincidences, besides electrons, comes from photons of the energy of about 10^8 eV. The estimation of the average number of electrons beneath the absorber corresponding to one photon over the absorber gives, for P_p, values between 0.4 and 0.6. Since the statistical error is very small, we assume that the limits given above define roughly the limit of error of the ratio p/e. So we accept $p/e = 0.70 \pm 0.15$, which value is concordant with that given by Milone and concerns the showers of the mean density of particles within the limits of 10 to 20 per sq. m. It is smaller than the value derived from the onedimensional theory of cascades. Most probably it is connected with a different mechanism of scattering of photons and electrons in extensive showers.

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CHEMISTRY

Hetero-Polyazeotropic Systems. II. Acetonitrile-*n*-Paraffinic Hydrocarbons

by

K. ZIĘBORAK and K. OLSZEWSKI

Presented by W. ŚWIĘTOSŁAWSKI on September 27, 1956

Introductory remarks

In a previous paper [1], the gradual transition from homoazeotropy, through homoazeo-heterozeotropy (azeotropic point lying outside the miscibility gap), to heterozeotropy was investigated in the series of binary systems formed by an azeotropic agent — methanol with the series of *n*-paraffins. In this paper the investigations are described in which the shapes of boiling temperature isobars of binary systems of acetonitrile with *n*-paraffins were examined by using the ebulliometric method. The phenomena observed are different from those observed in the previous investigations. This is due to the fact that the normal boiling temperature of acetonitrile (81.55°C.) is lower than the critical solution temperatures of all the binary systems examined.

Azeotropy in the acetonitrile-hydrocarbon systems has been investigated by Bishop and Denton [2] by the fractional distillation method. They determined the azeotropic parameters, but not the shapes of the boiling temperature isobars and liquid-liquid coexistence curves.

Experimental part. Preparation of substances

High-grade acetonitrile was distilled from phosphorus pentoxide through a column of 8-10 theoretical plates. Fractions boiling within 0.05° were collected. The hydrocarbons were obtained from synthetic gasoline fractions by treating them manyfold with concentrated sulphuric acid and then with soda-solution and water to remove the olefins. The fractions thus obtained were submitted to fractionation in the presence of calcium chloride. Table I contains the refractive indices and

the boiling temperatures of acetonitrile and of very narrow fractions of hydrocarbons, found by means of Świętosławski's ebulliometer.

TABLE I

Characteristics of the substances

	Boiling temp. °C.	Refractive index n_D^{20}
acetonitrile	81.55	1.3447
n-heptane	98.53	1.3875
n-octane	125.7	1.3980
n-nonane	150.0	1.4059
n-decane	174.1	1.4124
n-undecane	195.4	1.4185

The data indicate that the hydrocarbons, especially *n*-nonane and *n*-undecane, contained some amounts of isomers. It seems, however, that their influence on the results was very small.

Method of investigation

The boiling and the condensation temperatures were measured in a two-stage semi-micro ebulliometer [3]. Care was taken to avoid any contact of the substances with atmospheric moisture. The atmospheric pressure changes were controlled by the use of a simple ebulliometer filled with water. As the measurements were strictly comparative, the results were corrected to normal pressure. Critical solution temperatures were measured by the conventional Alexieyev method.

Results

Boiling temperature isobars, obtained for the binary systems of acetonitrile with hydrocarbons are shown in Fig. 1. The boiling temperature isobar of the acetonitrile-undecane system contains a horizontal section at a temperature higher than the boiling temperature of acetonitrile. The system belongs without any doubt to the heterozeotropic type. The next boiling temperature isobar formed by acetonitrile and *n*-decane has a minimum outside the miscibility curve. The system is therefore homoazeo-heterozeotropic. The isobars formed with *n*-nonane, *n*-octane, and *n*-heptane are characterised by flat minima, typical for heteroazeotropic systems. The data are summarised in Table II.

TABLE II

Data for the binary systems

System of acetonitrile with:	Boiling temp. of azeotrope or heteroze-otrope	Azeotropic depression °C. *)	Type of system	Crit. sol. temp. °C.	Crit. composition in mole per cent of hydrocarbon
n-undecane	81.85	+0.30	heterozeo-trope	112.5	23
n-decane	81.45	—0.10	homoazeo-heterozeo-trope	107.5	25
n-nonane	79.82	—1.73	heteroazeo-trope	100.0	30
n-octane	76.70	—4.85	„	91.5	33
n-heptane	69.55	—12.00	„	84.6	37

*) The positive sign corresponds to a heterozeotropic system

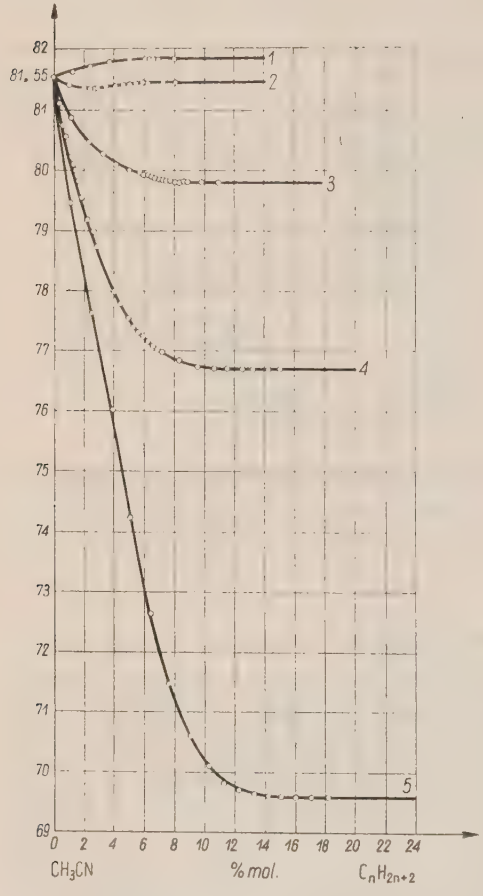
The results of investigations of mutual solubility of the components are collected in Table II and graphically represented in Fig. 2.

Discussion of the results

In the systems examined the transition is observed from heteroazeotropy to heterozeotropy. The mediate stage represents the homoazeoheterozeotropic system of acetonitrile with *n*-decane. All the systems differ considerably from those formed by methanol with *n*-paraffins [1]. The series fulfils to some extent the assumptions of Stecki who considered the regular solutions showing limited solubility [4]. Probably all the phenomena predicted by the theory would be observed, if additional data for systems with lower boiling hydrocarbons, e. g., *n*-hexane and *n*-pentane or their isomers, were available. The essential difference between the investigated systems and those theoretically considered by Stecki is that the upper critical solution temperatures undergo changes in the real series of systems. In spite of the increase of critical temperatures with increasing molecular weights of the hydrocarbons, the transition phenomena agree with the theory. This is due to the fact that the systems belong to the first class of the classification of heteropolyazeotropic systems, proposed by one of the authors [1].

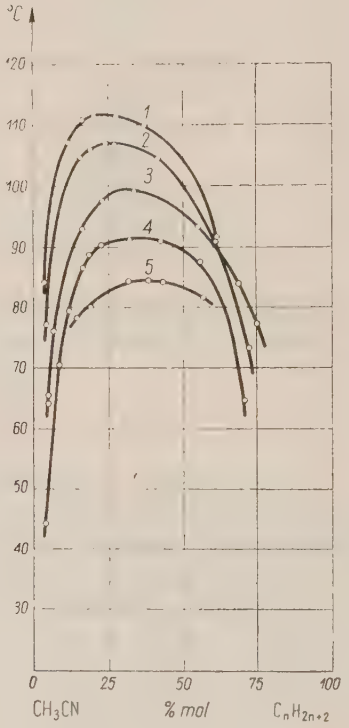
The data given in Table II indicate that the concentrations in mole per cent of hydrocarbons at the critical temperature decrease linearly with the increasing carbon chain length of the hydrocarbons. The critical temperature increases with the increase of the length of the hydrocarbon molecule. The relative critical temperature increase is the smaller, the larger the hydrocarbon molecule. An exception lies in the difference between the critical solution temperatures of mixtures of acetonitrile

with *n*-heptane and *n*-octane. This is probably due to the presence of some impurities which exert a great influence in that respect.



1. $CH_3CN-C_{11}H_{24}$; 2. $CH_3CN-C_{10}H_{22}$;
3. $CH_3CN-C_9H_{20}$; 4. $CH_3CN-C_8H_{18}$;
5. $CH_3CN-C_7H_{16}$; p=760 mm.

Fig. 1. Boiling temperature isobars of binary systems of acetonitrile with *n*-undecane (1), *n*-decane (2), *n*-nonane (3), *n*-octane (4), and *n*-heptane (5). Pressure 760 mm. of Hg



1. $CH_3CN-C_{11}H_{24}$; 2. $CH_3CN-C_{10}H_{22}$;
3. $CH_3CN-C_9H_{20}$; 4. $CH_3CN-C_8H_{18}$;
5. $CH_3CN-C_7H_{16}$.

Fig. 2. Mutual solubility curves of the systems of acetonitrile with *n*-undecane (1), *n*-decane (2), *n*-nonane (3), *n*-octane (4), and *n*-heptane (5)

The authors are greatly indebted to Professor W. Świętosławski for his helpful discussion of the phenomena examined.

Summary

1. The boiling temperature isobars of binary systems formed by acetonitrile with *n*-heptane, *n*-octane, *n*-nonane, *n*-decane and *n*-undecane were determined. Characteristic transition from heteroazeotropy to heterozeotropy was observed.

2. Critical solution temperatures of these systems were measured. Characteristic changes in critical temperatures and compositions have been noticed.

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[3] W. Świętosławski, *Ebulliometric Measurements* Reinhold Publ. Corp., New York, 1945.

[4] J. Stecki, in press.

TABLE DES MATIÈRES DU VOLUME IV

Mathématique

Astronomie

Physique Théorique

Physique Expérimentale

Chimie

Géologie

LISTE DES AUTEURS DU VOLUME IV

ERRATA AU VOLUME IV

Page/ligne	Au lieu de	Lire
1^{6}	M	$\overline{M}$
3^{7}	$\|u\|p/P, \quad \|v\|q/Q$	$\|u\|p/p, \quad \|v\|q/q$
110	Le texte indiqué sous la Fig. 3 se rapporte à la Fig. 4, et vice versa.	
207_{18}	A_1	A_i
207_{8}	*positive*	*integral*
208^{1}	positive number	integer
208^{6}	$M_Z(x)$	$M_Z(X)$
240^{3}	$+0\,(\|x-x_0\|)^n,$	$+0\,(\|a-x_0\|^n),$
241_{4}	$1/\|x\|^{\alpha}\sin 1/\|x\|^{\beta}$	$\|x\|^{-\alpha}\sin\|x\|^{-\beta}$
241_{4}	intégrales	intégrables
245^{11}	$\sum_{\nu=0}^{k}$	$\sum_{\nu=0}^{l}$
$251^{8,9,15}$	Rayer t dans les équations.	
251^{18}	Rayer t du côté gauche de l'equation.	
314^{11}	$a \in \mathfrak{P}$	$\mathbf{a} \in \mathfrak{P}$
316^{2}	$\mathbf{P}$	$\mathfrak{P}$
317^{10}	$\Gamma^i_{kl}\,\mathbf{df}\,(\delta_k \mathbf{g}_l, \mathbf{g}^i)\left(\frac{\delta \mathbf{g}_i}{\delta \mathbf{x}^k}, g^i\right)$	$\Gamma^i_{kl}\,\mathbf{df}\,(\delta_k \mathbf{g}_l, \mathbf{g}^i)$
317^{12-13}	$\sqrt{R^i_{kln}=0},$	$R^i_{kln}=0,$
318^{12}	$D\mathbf{x}^*=\mathbf{g}^{i_0 i_1 \dots i_n}\dots$	$D\mathbf{x}^*=(n+1)\,\mathbf{g}^{i_0 i_1 \dots i_n}\dots$
318^{13}	$=\mathbf{g}_{i_0 i_1 \dots i_n}$	$=(n+1)\,\mathbf{g}_{i_0 i_1 \dots i_n}$
319^{22}	$D^*\mathbf{a}=\mu f$	$D^*\mathbf{a}=\mu \mathbf{f}^*$
319^{21-22}	$a=a^*$	$\mathbf{a}=\overline{\mathbf{a}}$
322_{13}	$\triangle ABC \cong \triangle ABC',$	$\triangle ADC \cong ADC'$
322_{7}	$\triangle ACB \cong ACB,$	$\triangle ACD \cong ACD$
323^{7}	AB	AC
323^{20}	l'angle droit	l'angle droit A
405^{6}	gives a φ algebraic	gives an algebraic
405_{5}	$G=D+\sum_u^* J_n \Big/ \sum_j^* J_j,$	$G=D+\sum_\alpha^* J_{p\alpha} \Big/ \sum_\beta^* J_{p_\beta}$
428^{1}	$\cos^2\lambda$	$\sin^2\lambda$

Page/ligne	Au lieu de	Lire
428^{15}	$\cos^2 \lambda$	$\sin^2 \lambda$
428^{21}	$7 \cdot 10^{-14}$	$6 \cdot 10^{-18}$
442_7	$-\frac{1}{2} \overset{q}{_0} g_{00;ik}$	$-\frac{1}{2} \overset{l}{_l} g_{00;ik}$
454^{17}	$8 C^2_{1s,2}$	$8 C^2_{1s,1}$
455^{10}	$I_0 = 0$	$\delta I_0 = 0$
494^{23}	$C(R)$	$C(Q)$
500^{3}	$0 < \eta(x) \leqslant \delta(x)$	$0 < \eta(t,x) \leqslant \delta(t,x)$